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Environmental Degradation of Materials for Nuclear Waste Repositories Engineered Barriers

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Abstract

Several countries are considering geological repositories for the storage of nuclear waste. Most of the environments for these repositories will be reducing in nature, except for the repository in the US, which is going to be oxidizing. For the reducing repositories, alloys such as carbon steel, copper, stainless steels and titanium are being evaluated. For the repository in the US, some of the most corrosion resistant commercially available alloys are being investigated. This paper presents a summary of the behavior of the different materials under consideration for the repositories and the current understanding of the degradation modes of the proposed alloys in ground water environments from the point of view of general corrosion, localized corrosion and environmentally assisted cracking.

Keywords: *Nuclear Waste, Container Materials, Corrosion, Reducing, Oxidizing*

INTRODUCTION

Radioactive materials are widely used in various applications including medical, weapons and power generation. Once these materials lose their commercial value, they are considered radioactive waste. The wastes can be separated into two types, defense (weapons) and civilian (power, medical) [1]. Its safe disposal requires that the waste be isolated from the environment until radioactive decay has reduced its toxicity to innocuous levels for plants, animals, and humans. Many different types of radioactive waste are produced during commercial and defense nuclear fuel cycles. One type of waste, denoted high-level waste (HLW), contains the highest concentration of radiotoxic and heat-generating species. Because of this factor, the most stringent standards for disposing of radioactive wastes are being placed worldwide on HLW, and the majority of the radioactive waste management effort is being directed toward the HLW problem. One of the most common types of HLW is the spent fuel (SF) from commercial nuclear reactors for power generation.

All of the countries currently studying the options for disposing of HLW have selected deep geologic formations to be the primary barrier for accomplishing this isolation. It is postulated that by the very nature of these geological sites, they will contain the waste for long times, limiting their spread, for example, through water flow. [2] Most of the repository designs also

plan to delay the release of radionuclides to the environment by the construction of engineered barrier systems (EBS) between the waste and the geologic formation. The principal engineered component in this multibarrier approach is the waste package, which includes the waste itself, possibly a stabilizing matrix for the waste (together termed the wasteform), and a metallic container that encloses the wasteform. Beyond the metallic containers, other barriers could be added to attenuate the impact of the emplacement environment on the containers. There are more than thirty nations currently considering the geological disposal of HLW [2-5]. Twenty years ago most of the repository designs specified lifetimes from 300 to 1000 years. Currently, some of the minimum length of time specified for some repositories has increased to 10,000, 100,000 and even to 1,000,000 years [3-9]. The viability of extrapolating corrosion data from short term testing to long time performance has been addressed by some investigators [6,10]. Other researchers have proposed models to predict the lifetime performance of container alloys [11,12].

Environmental and Materials Considerations

The most common host rocks planned for nuclear waste repositories in the world are clay, basalt and granite [5]. The containers are intended to be placed in alcoves located at varying depth below the water table. The depth of emplacement may vary from country to country but it is generally assumed to be on the order of 100 to 500 meters. The only non-saturated (above the water table) environment for a repository is the one projected for the US, where the containers will be placed horizontally [8].

According to the value of the redox potential, the repository environment can be categorized as reducing or oxidizing. In a reducing redox potential, the cathodic reaction is controlled by the hydrogen discharge reaction. An oxidizing redox potential is established by the cathodic reactions other than hydrogen reduction, for example by the reduction of dissolved oxygen. Most of the repositories in the world will be reducing based on redox potentials, since they will rely on depth (where the solubility of oxygen in water is minimal) and a projected backfill with bentonite [5]. The intended function of the backfill is to retard the diffusion of oxygen towards the containers and the diffusion of the radionuclides away from the containers. The repository in the US will not have restrictions regarding the availability of oxygen to contact the containers, that is, the redox potential will be oxidizing in nature, provided an aqueous solution materializes. The groundwaters associated with the rock formations should all be relatively benign to most materials because of their low ionic strengths, near neutral pH, and low concentrations of halide ions [2]. The corrosivity of these waters could increase if significant groundwater vaporization occurs when high container temperatures exist during the early emplacement times. The container temperature may be influenced by the design and loading of the waste package, the density of waste package emplacement, and the thermal properties of the surrounding rock. Because heat is a significant by-product of HLW decay, the temperature of all waste containers will initially increase and then decrease as the activity of the waste decays. The predicted maximum temperature for waste packages emplaced in a consolidated volcanic ash (tuff) formation in the US is not expected to be higher than 160°C-200°C [8]. Typical maximum container temperatures for a number of other repository locations are expected to be lower than 100°C [2-3].

Except for the US, most of the recommended materials for the containers will be carbon steel, stainless steel, or copper [5]. Because these metals are not in the high end of the scale of

corrosion-resistant alloys, the emphasis of the design is on a controlled environment rather than on the performance of the material itself. The composition of candidate materials is given in Table 1.

REDUCING ENVIRONMENTS

The containers in reducing environments will be generally surrounded by a back fill of bentonite, which will greatly limit the availability of oxygen to the metal surface. The lack of oxygen (or other oxidizing species) will create a redox potential that will be closer to the hydrogen evolution reaction. Elements such as iron (Fe), nickel (Ni), and copper (Cu) are mostly in the range of corrosion immunity at these reducing potentials in the near neutral pH range [2,13]. The most common materials under study in typically reducing environments are carbon steel, stainless steel, copper, and titanium [2,5]. For the least corrosive underground waters, carbon steels could be viable materials; however, for the most saline conditions, titanium alloys are also being studied.

Carbon Steel and Low Alloy Steel. Carbon and low alloy steel have been extensively tested in ground water environments for the last 30 years. Corrosion rates measured for carbon steels in granitic waters ranged from 3 to 55 $\mu\text{m}/\text{yr}$, with one study showing that the rate reaches a maximum at around 80°C [14]. The conditions that would lead to localized corrosion of carbon steels are quite specific and unlikely to be present in typical granitic groundwaters [15]. However, hydrogen embrittlement and hydrogen blistering of low-alloys steels is possible in granitic environments with a high rate of hydrogen production [15]. Carbon steel will also have low corrosion rates in basaltic waters. Even in oxygenated solutions at 150°C, the corrosion rate of all tested carbon steels in basaltic waters was on the order of 100 $\mu\text{m}/\text{year}$.

Under the Swedish program, researchers have studied the anoxic corrosion behavior of carbon steel and cast iron in ground water at 50°C and 85°C and the impact of the presence of copper on the type and the mechanical properties of the films formed on the iron alloys [16]. They used a barometric cell filled with a simulated ground water and monitored the redox potential in the cell at 30°C on a gold electrode. They determined that when steel was introduced to the cell, the redox potential decreased rapidly due to the consumption of the residual oxygen by the corrosion of the steel [16].

As part of the Japanese program of nuclear waste disposal, the passive corrosion behavior of steels was found to be dependent on variables such as ground water pH, temperature and available dissolved oxygen [17]. Scientists in the Japanese program have raised the concern that whenever the corrosion of steel decreases due to a decrease in the oxygen content, the alkalinity in the immediacy of the steel increases. Since higher alkalinity would reduce the free corrosion potential of the steel, the process may increase the rate of hydrogen gas production that could be detrimental for the stability of the repository.

Carbon steel has also been identified as a candidate material for rock salt repositories in the German program. Studies were conducted to determine the corrosion response of welded and non-welded Fe1.5Mn0.5Si steel in a MgCl_2 rich brine (Q-brine) at 150°C under an irradiation field [18]. Welding was carried out by gas tungsten arc (GTAW) and electron beam (EB). The overall corrosion rate of both welded and non-welded materials was approximately 70 $\mu\text{m}/\text{yr}$; however, the welded materials experienced some localized attack in the weld seam area. When

the material was heat treated for 2 h at 600°C, the corrosion rate of the welded material increased by approximately 40% [18].

Carbon steel and low alloy steel have also been identified as candidate materials to contain nuclear waste for an intermediate storage of 100 years in the French program [19]. The dry oxidation testing of carbon steel in dry air (less than 15 ppm water), in air plus 2% water and in air plus 12% water at 300°C for up to 700 h showed little damage to the tested coupons. When the depth of the oxide layer was extrapolated to 100 years, it resulted in less than 150 µm of damage. The authors also noted little or nil water vapor effect on the oxidation rate at 300°C [19]. Recently, the commitment of the French program to adopt a 55 mm thick carbon steel wall for the container has been reaffirmed [20].

Copper. The container for the disposition of nuclear waste in Sweden will consist of a 50 mm thick layer of copper over cast nodular iron, which will provide the mechanical strength. Groundwater in granitic rock (as in the Swedish repository) is oxygen free and reducing below a depth of 200 meters. The redox potential is between -200 to -300 mV in the hydrogen scale and the pH ranges from 7 to 9 [21]. The chloride concentration in the groundwater can vary from 0.15 mM to 1.5 M with an equivalent amount of sodium and less calcium. The corrosion of a copper container in this reducing environment is expected to be less than 5 mm in 100,000 years of emplacement [21]. The corrosion of copper is mainly controlled by the availability of oxygen, sulfate, and sulfide in the groundwater. The failure time of the copper layer in the Swedish container has been modeled and it is predicted that the failure, both by general and pitting corrosion, would be higher than 10^6 years under realistic emplacement conditions [22]. The anodic behavior of copper was also studied as part of the Japanese nuclear waste disposal program using potentiodynamic polarization tests in simulated ground water at 30°C [23]. The amount of dissolved oxygen as well as different additions of chloride, sulfate, and bicarbonate was controlled. They concluded that both sulfate and chloride promote the active dissolution of copper while carbonate is a passivating agent [23].

In the Canadian design, the thickness of the external copper layer is 25 mm. Scientists have modeled the failure mechanism of copper as a function of the oxygen availability, the temperature, the salinity of the solution, and the redox potential. It is predicted that copper will undergo general corrosion and pitting during the initial warm and oxidizing period but only general corrosion during the subsequent longer anoxic cooler period. It has been predicted by this model that the Canadian copper container could last more than 10^6 years [24]. The long-term corrosion rates of many copper-base alloys are also sufficiently low, <20 µm/yr (0.78 mil/yr) at 200 °C, that their use now appears feasible. When a copper container is buried in a mostly reducing environment, the metal will initially be in contact with oxygen, until the oxygen is fully consumed, for example by corrosion [25,26,27].

It is known that copper may suffer environmentally assisted cracking (EAC) such as stress corrosion cracking (SCC) in waters containing for example ammonia and nitrite (NO_2^-). It has been shown that copper alloys, candidate materials for the Canadian waste containers, were susceptible to SCC using the slow strain rate technique [28]. It has been reported that the crack growth rate could be as high as 8 nm/s [29]. However, the conditions under which the damage occurred were extreme and unrepresentative of container emplacement conditions. In the actual container, the general absence of aggressive SCC species, the limited applied strain, and the limited supply of oxygen will limit the susceptibility to environmental cracking. In another study, it has been shown that the minimum stress intensity for crack propagation in copper for

the Swedish container was 30 MPa \sqrt{m} when tested in a 0.3 M NaNO₂ solution [30]. A stress intensity of 30 MPa \sqrt{m} can be considered high for a statically loaded container having shallow defects on the surface.

Stainless Steel and Nickel Alloys. The cyclic potentiodynamic polarization method (ASTM G 61) was used to evaluate the anodic behavior of corrosion resistant alloys in oxidized Boom clay water (in Belgium) with varying degrees of added chloride at 90°C [31]. The original Boom clay water is dominated by chloride and sulfate. The alloys studied included 316L SS (also with high Mo and with Ti) (S31603), Alloy 926 (N08926), Alloy 904L (N08904), Alloy C-4 (N06455) and Ti Gr 7 (R52400) (Table 1). It was found that both R52400 and N06455 resisted pitting corrosion even at added chloride concentrations of 10,000 ppm and N08926 resisted pitting up to 1000 ppm chloride. The other alloys showed minor pitting at 100 ppm chloride and definite pitting corrosion at the higher tested chloride concentrations [31].

Titanium. Titanium (Ti) alloys are under study as candidate materials for the containers in Canada, Japan, and Germany. The titanium alloys were selected as a potential alternative because of their excellent performance in more aggressive brine solutions compared for example to stainless steels. Corrosion rates for Ti Gr 2 and Ti Gr 12 in both oxygenated and irradiated basalt environments are very low—less than 2 $\mu\text{m/yr}$ (0.08 mil/yr). Failure models for the degradation of Ti Gr 2 have been published [32]. The model takes into account the crevice propagation rate as a function of temperature and oxygen availability as well as other factors such as the amount of hydrogen absorbed by the alloy during corrosion before a critical concentration for failure is reached [32]. The localized corrosion resistance of titanium alloys was widely investigated [33,34]. Testing showed that as the temperature and the chloride concentration increased, the repassivation potential ($E_{R,CREV}$) for Ti Gr 1 and Ti Gr 12 decreased to values well below the corrosion potential (E_{COR}) [33]. Ti Gr 12 was more resistant to crevice corrosion than Ti Gr 1. At constant temperature and chloride concentration, $E_{R,CREV}$ increased as the palladium (Pd) content in the alloy increased, rapidly up to 0.008% Pd and then slower between 0.008% to 0.062% Pd [34].

Titanium alloys were also investigated for their resistance to environmentally assisted cracking (EAC). One way by which titanium alloys may suffer EAC under reducing conditions is by the formation of hydrides. Slow strain rate testing was conducted using Ti Gr 1 in deaerated 20% NaCl at 90°C at an applied potential of -1.2 V (SHE) [35]. It was confirmed that cracks initiated as deep as the presence of hydrides, that is, the presence of hydride was necessary for cracks to initiate. Based on the critical cracking thickness and on the predicted amount of hydrogen generated, the authors dismissed the hypothesis that the containers may fail by cathodic EAC [35].

OXIDIZING ENVIRONMENTS

The design of the waste package for the Yucca Mountain repository has evolved in the last ten years [5,8]. Since 1998, the design specified a double walled cylindrical container covered by a titanium alloy drip shield. The outer shell of the container will be a Ni-Cr-Mo alloy (N06022) (Table 1), with an inner shell of austenitic Type 316 stainless steel (S31600). The function of the outer barrier is to resist corrosion and the function of the inner barrier is to provide mechanical strength and shield radiation. The drip shield will be made of Ti Gr 7 and a

higher strength Ti alloy (Ti Gr 29). The function of the drip shield is to deflect rock fall and early water seepage on the container [8].

Corrosion Behavior of Alloy 22 (N06022)

The container may suffer corrosion if water is present in sufficient amount at the repository site. Dry corrosion of Alloy 22 is negligible for the emplacement conditions. There are three main modes of corrosion that the container may suffer during its emplacement time. These are: (1) Uniform, general or passive corrosion, (2) Localized corrosion (e.g. crevice corrosion) and (3) Environmentally Assisted Cracking (e.g. stress corrosion cracking) [5,36]. All three types of corrosion may be influenced by the environment, including temperature, solution composition (chloride and nitrate concentration), redox potential.

Uniform and Passive Corrosion of Alloy 22. General corrosion (or passive corrosion) is the uniform thinning of the container alloy at its open circuit potential or corrosion potential (E_{corr}). In the presence of aerated multi-ionic brines, Alloy 22 is expected to remain passive at its E_{corr} . Passive corrosion rates of Alloy 22 in multi-ionic solutions simulating concentrated ground waters from pH 2.8 to 10 are in the order of 10 nm/year [5,37]. This low corrosion rate was measured for a range of E_{corr} from -100 mV to +400 mV SSC (saturated silver chloride electrode) at 60°C and 90°C.

The low corrosion rates or passive behavior of Alloy 22 is because of the formation of a protective, chromium rich oxide film between the alloy (metal) and the surrounding electrolyte. This passive film is even stable in the presence of strong mineral acids at temperatures below 60°C [38]. It has been shown that the thickness of this passive film could be in the range of 5 to 6 nm [39]. The long-term extrapolation of the corrosion rate of Alloy 22 has been modeled considering that the dissolution rate is controlled by the injection of oxygen vacancies at the oxide film/solution interface [40]. It has been concluded that it is unlikely that catastrophic failure of the container may occur due to long-term passive film dissolution [40].

Localized Corrosion of Alloy 22. Localized corrosion (e.g. crevice corrosion) is a type of corrosion in which the attack progresses at discrete sites or in a non-uniform manner. The degradation model assumes that localized corrosion will only occur when E_{corr} is equal or greater than a critical potential (E_{crit}) for localized corrosion [41]. That is, if $E_{\text{corr}} < E_{\text{crit}}$, only general or passive corrosion will occur. E_{crit} can be defined as a certain potential above which the current density or corrosion rate of Alloy 22 increases significantly and irreversibly above the general corrosion rate of the passive metal. The margin of safety against localized corrosion will be given by the value of $\Delta E = E_{\text{crit}} - E_{\text{corr}}$. The higher the value of ΔE , the larger the margin of safety for localized corrosion. It is important to note here that the values of both E_{corr} and E_{crit} may depend both on the metallurgical condition of the alloy and the environment such as temperature, chloride concentration, presence of inhibitors. E_{corr} is determined by measuring the long-term steady-state value of the open circuit potential in each environment of relevance. E_{crit} is the crevice repassivation potential [41].

Alloy 22 is extremely resistant to pitting corrosion but may suffer crevice corrosion especially in pure chloride solutions and at temperatures higher than 75°C [41-47]. The crevice corrosion susceptibility of Alloy 22 can be fully inhibited by the presence of other anions in solution [41-47]. The best inhibitor of crevice corrosion is nitrate [47].

Environmentally Assisted Cracking of Alloy 22. Wrought mill annealed (MA) Alloy 22 is highly resistant to EAC in most environments, including acidic concentrated and hot chloride solutions. Welded and non-welded U-bend specimens of Alloy 22 and other five nickel base alloys exposed for more than 5 years to multi-ionic solutions that represent concentrated ground water of pH 2.8 to 10 at 60°C and 90°C were free from EAC [48]. Even though Alloy 22 is resistant to EAC in concentrated hot chloride solutions, it may be susceptible under other severe environmental conditions. Slow strain rate tests were performed using MA Alloy 22 specimens in Simulated Concentrated Water (SCW) and other solutions as a function of the temperature and applied potential [49,50]. SCW has a pH 8-10 and it is approximately 1000 times more concentrated than ground water. Alloy 22 was found susceptible to EAC in hot SCW solutions and bicarbonate plus chloride solutions at anodic applied potentials approximately 300-400 mV more positive than E_{corr} . It was demonstrated that the most aggressive species for EAC in SCW was bicarbonate [50].

Corrosion Behavior of Titanium Alloys

Titanium grade 7 (Ti Gr 7 or R52400) was selected to fabricate the detached drip shield for the repository in Yucca Mountain [8]. Other Ti alloys of higher strength such as Ti Gr 29 may also be used for the structural parts of the drip shield. The presence of the drip shield would deflect early water seepage from the containers. This drip shield would also deflect rock fall from the containers. Ti Gr 7 belongs to a family of Ti alloys especially designed to withstand aggressive chemical environments (Table 1) [51]. The superior corrosion resistance of Ti and Ti alloys is due to a thin, stable and tenacious oxide film that forms rapidly in air and water, especially under oxidizing conditions. A detailed review of the general, localized and environmentally assisted cracking behavior of Ti Gr 7 and other titanium alloys relevant to the application in Yucca Mountain has addressed, among other topics, the effect of alloyed palladium, the properties of the passive films, and the effect of radiation [52]. The presence of fluoride may render Ti Gr 7 more susceptible to general and crevice corrosion under anodic polarization [53].

Weight-loss, creviced, and U-bend specimens of Ti Gr 7, 12 and 16 were exposed to three different electrolyte solutions simulating concentrated ground water for over five years both at 60°C and at 90°C in the vapor and liquid phases of these solutions [54]. Ti Gr 7 generally exhibited the lowest corrosion rates irrespective of temperature or solution type while Ti Gr 12 generally exhibited the highest corrosion rates [54]. Titanium and Ti alloys may suffer environmentally assisted cracking (EAC) such as hydrogen embrittlement (HE). Embrittlement by hydrogen is a consequence of absorption of atomic hydrogen by the metal to form hydrides [55]. This may happen in service when the Ti alloy is coupled to a more active metal in an acidic solution. A critical concentration of hydrogen in the metal may be needed for HE to occur [52]. Stress corrosion cracking was reported in Ti Gr 7 specimens subjected to constant load tests in a concentrated ground water solution pH ~ 10 at 105°C [56]. Results from up to 5-year immersion testing at 60°C and 90°C of U-bend specimens made of wrought and welded Ti Gr 7 and Ti Gr 16 alloys showed that these alloys were free from environmentally assisted cracking (EAC) in multi-ionic solutions that could be representative of concentrated ground water [57]. Welded Ti Gr 12 U-bend specimens suffered EAC in SCW liquid at 90°C. Under the same conditions, non-welded Ti Gr 12 was free from cracking [57].

SUMMARY

1. Several countries are developing geologic repositories for their high-level nuclear waste
2. Most of the repositories in the world are planned to be in stable rock formations (e.g. granite) below the water table (saturated). The US is studying a repository above the water table (unsaturated)
3. The repositories will consist of a stable geologic formation within which engineered barriers will be constructed. The most important part of the engineered barrier is the container for the waste
4. The containers are in general designed as double walled metallic cylinders
5. From the corrosion point of view, most repositories will have reducing environments. One planned repository will have a natural oxidizing environment
6. Copper, titanium, stainless steels, and carbon steels were determined to be suitable materials for the reducing repositories.
7. Alloy 22 and Ti Gr 7 are being characterized for the mostly dry and oxidizing environment of the US repository.
8. Materials for the engineered barriers are being evaluated for general corrosion, localized corrosion, and environmentally assisted cracking resistance
9. The metals are studied under different metallurgical conditions, such as mill annealed, welded and thermally aged
10. Some of the most important environmental variables that may affect the corrosion behavior of the engineering materials include the concentration and type of the aqueous electrolytes at the site, temperature and redox potential.

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Table 1. Approximate Chemical Composition (in weight percent – wt%) for Studied Alloys

Alloy	UNS	ASTM	Cr	Cu	Fe	Mo	Ni	Ti	Other
Gray cast iron	F10001-F10012	A319-A159			~95 (bal)				3-3.5 C, 2-2.4 Si, 0.8 Mn
1018 carbon steel	G10180	A29			~98 (bal)				0.18 C, 0.5 Mn
4130 alloy steel	G41300	A29	1.0		~97 (bal)	0.2			0.3 C, 0.5 Mn
2.25Cr-1Mo	K30736	A213	2.25		bal	1			0.05 C, 0.4 Mn, 0.2 V
90–10 cupronickel	C70600	B111		~88 (bal)	1.3		10		1 max Mn, 1 max Zn
Type 304	S30400	A182	19		~70 (bal)		9		2 max Mn, 1 max Si
Type 316	S31600	A182	17		67 (bal)	2.5	12		2 max Mn, 1 max Si
Type 416	S41600	A194	13		~85 (bal)	0.6 max			1.25 max Mn, 1 max Si
Monel 400	N04400	B127		~32 (bal)	2.5 max		66.5		2 max Mn
Incoloy 825	N08825	B163	21.5	2.2	~30 (bal)	3.0	42	0.9	1 max Mn, 0.5 max Si
Inconel 625	N06625	B366	21.5		5 max	9.0	~60 (bal)	0.2	4 Nb, 0.5 max Mn
Hastelloy C-276	N10276	B575	16		5	16	~60 (bal)		4 W, 2.5 max Co
Hastelloy C-4	N06455	B575	16		3 max	16	~65 (bal)		2 max Co
Hastelloy C-22	N06022	B575	22		4	13	~57 (bal)		3 W, 2.5 max Co
Ti Gr 2	R50400	B265			0.3 max			~99 (bal)	0.25 max O
Ti Gr 7	R52400	B265			0.3 max			~98 (bal)	0.2 Pd, 0.25 max O
Ti Gr 16	R52402	B265			0.3 max			~98 (bal)	0.06 Pd, 0.25 max O
Ti Gr 12	R53400	B265			0.3 max	0.3	0.8	~98 (bal)	0.25 max O
Ti Gr 29	R56404	B265			0.25 max			~90 (bal)	6Al, 4V, 0.08-0.14 Ru